

Title: Novel High Energy Density Composite Cathode Materials for Lithium Rechargeable Batteries

Abstract

Lithium and manganese rich oxide cathode materials form a structurally integrated nanocomposite of Li_2MnO_3 and LiMO_2 (where $\text{M}=\text{Co},\text{Ni}$ and Mn) by sharing a common oxide lattice. We have demonstrated that the electrochemical performance of these cathode materials depends on various interrelated factors. Through extensive structural and electrochemical characterization, we have found that (i) a significant structural change occurs during first cycle, (ii) a relatively slower and continuous structural change occurs during repeated cycling and (iii) an electronically insulating solid electrolyte interface layer grows with repeated charge-discharge cycling. All these factors significantly influence the electrochemical performance of the cathode material. Various approaches have been adopted to improve the electrochemical performances of the nanocomposite $x\text{Li}_2\text{MnO}_3-(1-x)\text{Li}(\text{Mn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25})\text{O}_2$ ($0.0 \leq x \leq 1.0$) cathode materials. First, the composition of the integrated cathode and process parameters are optimized to yield high discharge capacity. Thus a discharge capacity of $\sim 300 \text{ mAhg}^{-1}$ is obtained in $x=0.5$ cathode. A layered to spinel conversion is identified in cathodes with higher Li_2MnO_3 content. Second, we have modified these integrated cathodes by partially dope oxygen with fluorine. Although the discharge capacity is found to be systematically reduced with the increase in fluorine content, both the cycleability as well as the rate capability is found to be improved in 0.02 mole fluorine doped integrated cathodes. Third, much better improvement in electrochemical properties is achieved in zirconium oxide coated integrated cathode materials. Though initial discharge capacity decreases with the increase in ZrO_2 content, both the capacity retention with cycling and rate performance have been significantly improved in zirconia modified samples as compared to their unmodified counterpart. It is found that the capacity fading of these integrated cathodes correlates well with the systematic increase of interfacial resistance of the cathode particles. We have demonstrated that the porous particulate ZrO_2 coating improved the capacity retention of these integrated cathodes by suppressing the impedance growth at the electrodes-electrolyte interface. Finally, we have studied the effect of particle size on the electrochemical performance of the integrated cathode materials and found that among several interrelated factors (viz. cathode composition, activation of Li_2MnO_3 component, crystallinity of the cathode particles etc.) an optimum particle size is very much crucial for the improved performance of the synthesized cathode materials.